

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 October 2003 (09.10.2003)

PCT

(10) International Publication Number
WO 03/083020 A2

(51) International Patent Classification⁷: **C10M**

(21) International Application Number: **PCT/US03/11199**

(22) International Filing Date: **28 March 2003 (28.03.2003)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
60/368,354 28 March 2002 (28.03.2002) US
60/441,012 17 January 2003 (17.01.2003) US

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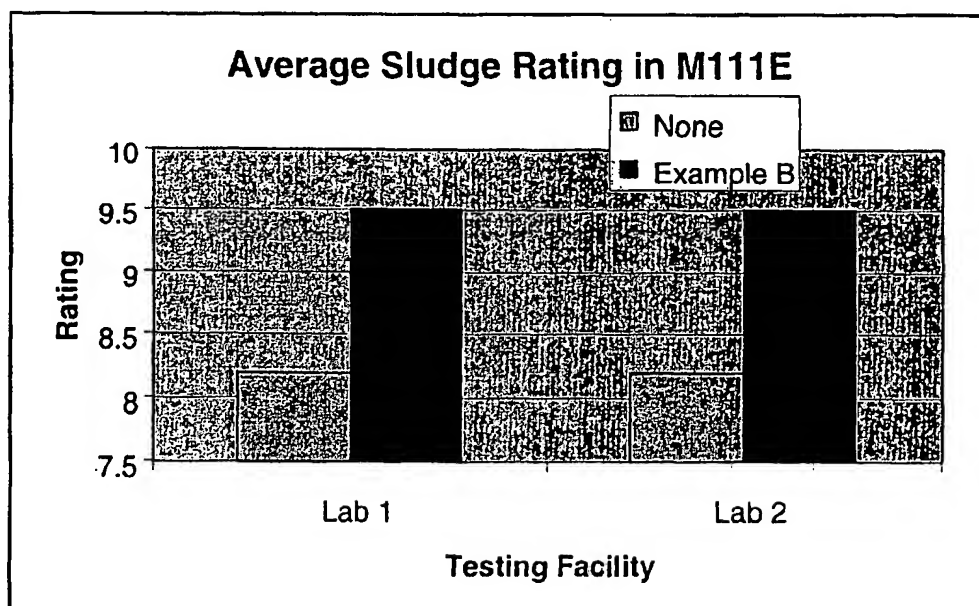
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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

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(54) Title: **METHOD OF OPERATING INTERNAL COMBUSTION ENGINE BY INTRODUCING DETERGENT INTO COMBUSTION CHAMBER**



(57) Abstract: In a method operating an internal combustion engine, a nitrogen-containing detergent composition is introduced into a combustion chamber of the engine wherein the detergent composition can improve the performance of both a fuel composition and a lubricating oil of the engine. The detergent composition contains (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine, (B) a hydrocarbyl-substituted amine, (C) a Mannich reaction product, (D) a high molecular weight polyetheramine, or (E) a mixture thereof.

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Published:

— without international search report and to be republished upon receipt of that report

(84) **Designated States (regional):** European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE: METHOD OF OPERATING INTERNAL COMBUSTION ENGINE BY
INTRODUCING DETERGENT INTO COMBUSTION CHAMBER

This application claims the benefit of U.S. Provisional Application Nos. 60/368354 filed
5 28 March 2002 and 60/441012 filed 17 January 2003.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention comprises a method of operating an internal combustion
10 engine that comprises introducing a nitrogen-containing detergent composition into a
combustion chamber during the operation of the engine. The method results in improved
performance of a lubricating oil of the engine and also improves performance of a fuel
composition when the detergent composition is present in the fuel composition.

2. Description of the Related Art

15 Current and future performance requirements and exhaust emission requirements
for internal combustion engines are necessitating new and improved lubricating oil
formulations and methods of lubrication for engines.

Longer intervals between engine oil drains lessen demands for disposal and effects
on the environment, but increase performance requirements for oxidation, wear,
20 detergency, dispersancy, viscosity stability and friction durability. Compression-ignited
diesel engines and spark-ignited direct injection engines have exhaust gas recirculation
(EGR) systems that reduce generation of nitrogen oxides (NO_x), by reducing the oxygen
concentration and consequently the combustion temperature, but that increase the
generation of soot in the lubricating oil. This increased soot requires increased
25 dispersancy, detergency and wear performance or more frequent oil drains to avoid severe
problems of wear, deposits and exhaust emissions. Formulating an engine lubricating oil
with increased amounts of additives to meet increased performance requirements is not
always possible due to limitations such as allowable sulfur, phosphorus and metal content
as well as performance issues from high levels of additives such as seal compatibility with
30 high levels of dispersants.

Spark-ignited gasoline engines and compression-ignited diesel engines have
various exhaust treatment devices to reduce emissions of carbon monoxide, hydrocarbons,

nitrogen oxides and particulates. Since it is believed that sulfur, phosphorus and metals can adversely affect engine exhaust treatment devices such as catalytic converters, a gradual reduction in the level of sulfur, phosphorus and metals in engine lubricating oils is being implemented. This reduction in sulfur, phosphorus and metals consequently
5 requires increased detergency, oxidation and wear performance from additives that do not contain sulfur, phosphorus or metals.

Fuels with reduced levels of sulfur for both spark-ignited and compression-ignited engines are also being introduced that are more compatible with exhaust treatment devices for reducing air pollutants. However, this reduction of sulfur levels in fuels can require
10 increased oxidation performance in lubricating oils.

U.S. Application No. 60/368,354 filed on March 28, 2002, discloses introduction of nitrogen-containing detergents including polyetheramines into the combustion chamber of an internal combustion engine to improve the performance of the lubricating oil.

U.S. Application No. 60/374,640 filed on April 23, 2002, discloses use of an
15 antioxidant in the fuel of an internal combustion engine to improve the performance of the lubricating oil.

European Publication No. EP1132455 A1 discloses a fuel additive composition of a Mannich condensation product and a hydrocarbyl-substituted polyoxyalkylene amine that controls engine oil screen plugging.

U.S. Patent No. 6,224,642 discloses the combination of a polyetheramine
20 $\text{RO}(\text{C}_4\text{H}_8\text{O})_n\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and a second compound that is a fatty acid, derivative of a fatty acid, or a succinic acid or anhydride where the combination is useful in fuels to reduce engine wear.

International Publication No. WO 01/88069 A1 discloses entrainment of metal
25 detergents and nonmetal detergents in the combustion chamber during operation of the engine to improve engine operation.

International Publication No. WO 97/44414 discloses the addition of a detergent and combustion improver to a fuel to reduce liner lacquering in a marine diesel engine.

International Publication No. WO 02/18521 A2 discloses that a lubricating oil can
30 have a phosphorus level of 0.05% by weight and satisfactory wear performance in conjunction with a gasoline fuel having a sulfur content below 10 ppm by weight.

International Publication No. WO 02/079353 discloses a) a gasoline additive concentrate composition containing a solvent, an alkoxylated fatty amine, and a partial ester having at least one free hydroxyl group and formed by reacting a fatty carboxylic acid and a polyol, b) a fuel composition containing gasoline and the concentrate composition, and c) a method of operating a gasoline internal combustion engine by
5 fueling the engine with the fuel composition which reduces fuel consumption.

It has now been found that the introduction of a nitrogen-containing detergent composition into a combustion chamber of an internal combustion engine improves the performance of a lubricating oil of the engine and also of a fuel composition when the
10 detergent composition is present in the fuel composition.

SUMMARY OF THE INVENTION

It is an object of the present invention to improve the performance of both a fuel composition and a lubricating oil of an internal combustion engine.

Another object of this invention is to improve the performance a fuel composition
15 and a lubricating oil of a compression-ignited or spark-ignited direct injection internal combustion engine having an exhaust gas recirculation system.

A further object of the invention is to improve the performance of a fuel composition and a lubricating oil of a spark-ignited or compression-ignited internal combustion engine having an exhaust treatment device and a lubricating oil that has at
20 least one of the properties selected from the group consisting of a phosphorus content below 0.1% by weight, a sulfur content below 0.5% by weight, and a sulfated ash content below 1.5% by weight.

An additional object of the present invention is to improve the performance of a fuel composition and a lubricating oil of a spark-ignited or compression-ignited internal
25 combustion engine having an exhaust treatment device and where a fuel of the fuel composition has a sulfur content below 80 ppm by weight.

Yet another object of this invention is to improve the performance of a fuel composition and a lubricating oil of a spark-ignited or compression-ignited internal combustion engine that is installed in a motor vehicle and has a recommended drain
30 interval for the lubricating oil of the engine of greater than 6,000 miles.

Yet a further object of the invention is to improve the performance of a fuel composition and a lubricating oil of a spark-ignited or compression-ignited internal

combustion engine that is a stationary engine having a recommended drain interval for the lubricating oil of the engine of greater than 150 operational hours.

Additional objects and advantages of the present invention will be set forth in the Detailed Description that follows and, in part, will be obvious from the Detailed
5 Description or may be learned by the practice of the invention. The objects and advantages of the invention may be realized by means of the instrumentalities and combinations pointed out in the appended claims.

To achieve the foregoing objects in accordance with the invention, as described and claimed herein, a method of operating an internal combustion engine comprises
10 introducing a nitrogen-containing detergent composition that comprises (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine; (B) a hydrocarbyl-substituted amine; (C) a Mannich reaction product of a hydrocarbyl-substituted hydroxy-containing aromatic compound, an aldehyde, and an amine; (D) a high molecular weight polyetheramine prepared by reacting one unit of a hydroxy-containing hydrocarbyl
15 compound with two or more units of butylene oxide to form a polyether intermediate, and aminating the polyether intermediate by reacting the polyether intermediate with an amine or with acrylonitrile and hydrogenating the reaction product of the polyether intermediate and acrylonitrile; or (E) a mixture thereof into a combustion chamber of the engine during the operation of the engine wherein the detergent composition improves the performance
20 of a lubricating oil of the engine.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows end of test total base number retention for 0W30 oil from VW fleet trial.

Figure 2 shows end of test total base number retention for 5W40 oil from VW fleet
25 trial.

Figure 3 shows average piston ratings for engine oils from VW fleet trial.

Figure 4 shows change in particulate emissions from VW fleet trial.

Figure 5 shows total base number retention for engine oils from Ford Crown Victoria fleet trial.

Figure 6 shows distance accumulated for TBN-TAN cross-over for engine oils
30 from Ford direct injection fleet trial.

Figure 7 shows particulate emissions for ISO8178 test cycle from Liebherr 914T engine test.

Figure 8 shows particulate emissions in 20-200 nm size spectrum for ISO8178 test cycle from Liebherr 914T engine test.

5 Figure 9 shows engine oil sludge ratings from M-B M111E engine test.

DETAILED DESCRIPTION OF THE INVENTION

A method of the present invention of operating an internal combustion engine comprises introducing a nitrogen-containing detergent composition that comprises (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine; (B) a hydrocarbyl-substituted amine; (C) a Mannich reaction product of a hydrocarbyl-substituted hydroxy-containing aromatic compound, an aldehyde, and an amine; (D) a high molecular weight polyetheramine prepared by reacting one unit of a hydroxy-containing hydrocarbyl compound with two or more units of butylene oxide to form a polyether intermediate, and aminating the polyether intermediate by reacting the polyether intermediate with an amine or with acrylonitrile and hydrogenating the reaction product of the polyether intermediate and acrylonitrile; or (E) a mixture thereof into a combustion chamber of the engine during the operation of the engine wherein the detergent composition improves the performance of a lubricating oil of the engine.

The internal combustion engine of the present invention includes all types of spark-ignited and compression-ignited engines to include those that can operate on a two-stroke or a four-stroke cycle. These internal combustion engines can be used in various types of motor vehicles and stationary and mobile or transportable equipment to include automobiles, trucks, off-highway vehicles and equipment, boats and ships, railroad engines, airplanes, recreational vehicles, generators, pumps, compressors, chain saws, mowers, and farm vehicles and equipment.

The method of the present invention of operating an internal combustion engine involves introducing a detergent composition into a combustion chamber of the engine. In one embodiment the detergent composition is introduced into the combustion chamber by injection from a dosing system. The injection from the dosing system can be directly into the combustion chamber or into a fuel system of the engine such as a fuel storage tank of the fuel system so that the detergent composition enters the combustion chamber as a component of a fuel composition. In other embodiments of the invention the detergent

composition is introduced into the combustion chamber as a component of the fuel composition where the detergent composition is added to a fuel in a bulk treatment at a refinery or storage facility or is added to a fuel in an aftermarket treatment such as adding the detergent composition to a fuel in a fuel tank of a motor vehicle.

5 The introduction of the detergent composition into a combustion chamber of an internal combustion engine improves the performance of a lubricating oil of the engine and also the performance of a fuel composition when the detergent composition is a component of the fuel composition. Improving the performance of the fuel composition can include deposit control in keeping clean or cleaning up deposits throughout the fuel
10 system to include intake valves, fuel injectors and combustion chambers; enhancing lubricity so that wear is reduced of fuel system components such as fuel pumps and fuel injectors; and reduction of particulate emissions. Improving the performance of the lubricating oil can include detergency such as acid neutralization or TBN (total base number) retention, dispersancy to include control of engine sludge and piston cleanliness,
15 antioxidation, antiwear, viscosity control and friction durability.

 In one embodiment of the invention the detergent composition is (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine. Throughout this application the term hydrocarbyl represents a univalent group of one or more carbon atoms that is predominately hydrocarbon in nature, but can contain heteroatoms such as oxygen
20 in the carbon chain and can have nonhydrocarbon and heteroatom-containing groups such as hydroxy, halo, nitro and alkoxy attached to the carbon chain. The hydrocarbyl substituent of the acylating agent can be a hydrocarbon group having a number average molecular weight of 150 to 5000 and in other instances of 175 to 3000 and 200 to 1500. The hydrocarbon group can be derived from an olefin or polyolefin. Virtually any
25 compound containing an olefinic bond may be used to react with a monounsaturated carboxylic acid reactant or equivalent thereof. The polyolefin can be derived from olefin monomers to include C₂ to C₂₀ monoolefins and in another instance C₂ to C₅ monoolefins. Useful monoolefins include ethylene, propylene, butenes such as isobutylene and 1-butene, pentenes, hexenes octenes and decenes. The polyolefin can be a homopolymer
30 prepared from a single olefin monomer such as a polyisobutylene or a copolymer prepared from a mixture of two or more olefin monomers such as copolymers of ethylene and propylene, 1-butene and isobutylene, and propylene and isobutylene. In an embodiment

of the invention the polyolefin is a polyisobutylene having a vinylidene double bond content of 50 to 70% and in another instance of 50 to 95%. Polyolefins can be prepared from olefin monomers by well known polymerization methods and are also commercially available.

5 The acylating agent can be derived from a monounsaturated monocarboxylic or polycarboxylic acid or reactive equivalent thereof. Reactive equivalents include acid anhydrides, esters, and acid halides. Useful monounsaturated monocarboxylic acids or reactive equivalents thereof include C₃ to C₁₀ acids and reactive equivalents such as acrylic acid, methacrylic acid and methyl acrylate. Useful monounsaturated
10 polycarboxylic acids and reactive equivalents thereof include C₄ to C₁₀ acids and reactive equivalents such as maleic acid, maleic anhydride, fumaric acid and dimethyl fumarate.

 The hydrocarbyl-substituted acylating agent can be prepared by reacting a polyolefin and a monounsaturated monocarboxylic and/or polycarboxylic acid or reactive equivalent thereof by well known methods such as the thermal reaction of a
15 polyisobutylene and maleic anhydride with or without chlorination as described in U.S. Patent No. 4,234,435.

 The amine of the detergent composition (A) can be any compound that contains a reactive nitrogen to hydrogen or N-H bond. The amine can be ammonia, a monoamine, a polyamine, or a mixture thereof. The monoamine and polyamine and ammonia also
20 include alkanolamines having one or more hydroxyl groups. In another embodiment of the invention an alcohol can also be present with the amine in a reaction with the hydrocarbyl-substituted acylating agent. The alcohol can be a monohydric alcohol such as butanol or a polyhydric alcohol such as ethylene glycol or pentaerythritol. Useful amines include hydroxylamine, ethanolamine, diethanolamine, butylamine, ethylenediamine, hydrazines,
25 polyethylenepolyamines such as tetraethylenepentamine, and polyethylenepolyamine bottoms. The amines are generally commercially available.

 The detergent composition (A) can be prepared by reacting the hydrocarbyl-substituted acylating agent and the amine at elevated temperatures such as the reaction of a polyisobutenylsuccinic acylating agent and a polyethylenepolyamine, for example,
30 polyisobutenylsuccinic anhydride and tetraethylenepentamine, at 100 to 200°C as described in U.S. Patent No. 4,234,435. In an embodiment of the invention the detergent composition (A) is a reaction product of a polyisobutenylsuccinic anhydride prepared from

a high vinylidene content polyisobutylene and a polyethylenepolyamine such as tetraethylenepentamine where the reaction product has a high imide content as described in International Publication No. WO02/102942. In another embodiment of the invention the detergent composition (A) is a reaction product of a hydrocarbyl-substituted acylating agent and a polyamine where the hydrocarbyl-substituted acylating agent is prepared from a reaction of an oxoalkanoic acid or reactive equivalent thereof such as glyoxylic acid or glyoxylic acid methyl ester methyl hemiacetal or pyruvic acid and a polyolefin such as a polyisobutylene as described in U.S. Patent No. 5,696,067. In a further embodiment of this invention the detergent composition (A) is a reaction product of a hydrocarbyl-substituted acylating agent and a polyamine where the hydrocarbyl-substituted acylating agent is prepared from a reaction of an oxoalkanoic acid or reactive equivalent thereof as just described above and a C₄ to C₁₄₅ alkylphenol as described in U.S. Patent No. 5,336,278. In still another embodiment of the invention the detergent composition (A) is the reaction product of a C₁₂ to C₂₀ alkenylsuccinic anhydride such as hexadecenylsuccinic anhydride and an alkanolamine such as N,N-diethylethanolamine. In yet a further embodiment of the invention the detergent composition (A) is a product of a mixture of a first and second polyisobutenylsuccinic anhydride, where the polyisobutenyl substituents have respectively number average molecular weights of 2300 and 1000, reacted with ethylene glycol and then reacted with N,N-dimethylethanolamine in a mole ratio of respectively 2:1:2.

The detergent composition of the present invention can be (B) a hydrocarbyl-substituted amine. The hydrocarbyl substituent of the amine can have a number average molecular weight of 150 to 5000 and in other instances of 175 to 3000 and 200 to 1500. The hydrocarbyl substituent can be derived from an olefin or a polyolefin as described above for the hydrocarbyl-substituent of the detergent composition (A). Useful polyolefins include polyisobutylenes. The amine of the hydrocarbyl-substituted amine can be derived from ammonia, a monoamine, a polyamine, or a mixture thereof. The monoamine or polyamine can be an alkanolamine having one or more hydroxyl groups. Useful amines include polyamines such as ethylenediamine and diethylenetriamine and alkanolamines such as 2-(2-aminoethylamino)ethanol. The detergent composition (B) can be prepared by several methods. In one embodiment of the invention polyisobutylene is chlorinated and the chlorinated polyisobutylene is reacted with an amine such as

ethylenediamine in the presence of a base such as sodium carbonate as described in U.S. Patent No. 5,407,453. In another embodiment of the invention a polyisobutylene is hydroformylated, for example, via the Oxo process, with carbon monoxide and hydrogen using a metal catalyst at an elevated temperature and pressure, and the product from the hydroformylation is aminated optionally in the presence of hydrogen as described in U.S. Patent No. 5,496,383. In a further embodiment of the invention a polyisobutylene is oxidized to an epoxide by one of several known methods such as oxidation with a peroxycarboxylic acid, and the epoxide is aminated generally with an excess of an amine as described in European Publication No. EP-B-573578. In still another embodiment of the invention the detergent composition (B) is a hydroxyalkyl-substituted fatty amine which can be represented by the formula $RN[(A^1O)_xH][(A^2O)_yH]$. R can be a C_{12} to C_{30} hydrocarbyl group and in other instances can be a C_{14} to C_{26} and a C_{16} to C_{22} hydrocarbyl group. The hydrocarbyl group can be a straight chain, a branched chain, or a mixture thereof. The hydrocarbyl group can be saturated, unsaturated, or a mixture thereof. A^1 and A^2 are independently C_2 to C_{18} alkylene groups and in other instances are C_2 to C_{12} and C_2 to C_8 alkylene groups where x and y are independently integers having a value of 0 or higher and x + y is at least 1 and in other instances x + y is 2 or greater than 2. The hydroxyalkyl-substituted fatty amine can be prepared by reacting one unit of a fatty amine with one or more units of an alkylene oxide to produce a monoalkoxylated and/or polyalkoxylated fatty amine. The alkylene oxide can be a C_2 to C_{18} alkylene oxide or a mixture of two or more C_2 to C_{18} alkylene oxides. Useful alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, or a mixture thereof. Useful hydroxyalkyl-substituted fatty amines include diethoxylated tallowamine, diethoxylated oleylamine, diethoxylated stearylamine and diethoxylated amines from soybean oil fatty acids which are commercially available such as the Ethomeen® series from Akzo Nobel.

The detergent composition of the present invention can be (C) a Mannich reaction product of a hydrocarbyl-substituted hydroxy-containing aromatic compound, an aldehyde, and an amine. The hydrocarbyl substituent of the aromatic compound can have a number average molecular weight of 120 to 3000 and in other instances the number average molecular weight can be 130 to 2300, 140 to 1500, 140 to 950, and 1000 to 2300. The hydrocarbyl substituent can be derived from an olefin or polyolefin as described above for the hydrocarbyl substituent of the acylating agent of detergent composition (A).

Useful polyolefins for the hydrocarbyl substituent of detergent composition (C) include a polyisobutylene, a polyisobutylene having a vinylidene double bond content of 50% or greater, and a polypropylene such as a C₁₂ polypropylene. The hydroxy-containing aromatic compound of the Mannich reaction product can include phenol, a polyhydroxy-
5 containing aromatic compound such as resorcinol and catechol, a C₁ to C₈ alkyl-substituted hydroxy-containing aromatic compound such as ortho-cresol, or a mixture thereof. The hydrocarbyl-substituted hydroxy-containing aromatic compounds can be prepared by well known methods such as for example a Lewis acid catalyzed alkylation of phenol with a polyisobutylene. The aldehyde of the Mannich reaction product can be a C₁
10 to C₇ aldehyde to include formaldehyde in one of its reactive forms such as formalin and paraformaldehyde. The amine used to prepare the Mannich reaction product contains at least one reactive nitrogen to hydrogen or N-H bond and can be ammonia, a monoamine, a polyamine, or a mixture thereof. The amine can be an alkanolamine containing one or more hydroxyl groups. Useful amines include ammonia, hydroxylamine, ethylamine,
15 dimethylamine, ethanolamine, diethanolamine, ethylenediamine, dimethylaminopropylamine, and polyethylenepolyamines. The Mannich reaction product can be prepared by reacting a hydrocarbyl-substituted hydroxy-containing aromatic compound, an aldehyde, and an amine at an elevated temperature such as for example an alkylphenol derived from a high vinylidene polyisobutylene, formaldehyde and ethylenediamine as described in U.S. Patent No. 5,697,988.
20

The detergent composition of the present invention can be (D) a high molecular weight polyetheramine. This polyetheramine can contain two or more ether units and is generally prepared from a polyether intermediate. The polyether intermediate can be a reaction product of one unit of a hydroxy-containing hydrocarbyl compound with two or
25 more units of butylene oxide. The hydroxy-containing hydrocarbyl compound can be an alcohol or an alkyl-substituted phenol where the alcohol or alkyl substituent of the phenol can have 1 to 50 carbon atoms, 6 to 30 carbon atoms in a second instance, and 8 to 24 carbon atoms in a third instance. The alcohol or alkyl substituent of the phenol can have a straight carbon chain, branched carbon chain, or a mixture thereof. The hydroxy-
30 containing hydrocarbyl compound can contain one or more hydroxyl groups.

The polyether intermediate from the reaction of a hydroxy-containing hydrocarbyl compound and butylene oxide can have 2 to 100 repeating butylene oxide units, 5 to 50

repeating butylene oxide units in a second embodiment, and 15 to 30 repeating butylene oxide units in a third embodiment. U.S. Patent No. 5,094,667 provides reaction conditions for preparing a polyether intermediate.

The high molecular weight polyetheramine of the present invention can be prepared from the above described polyether intermediate that is prepared from butylene oxide.

In one embodiment of the invention the polyetheramine is prepared by reacting the polyether intermediate derived from butylene oxide with acrylonitrile to form a nitrile that is then hydrogenated to form a 3-aminopropyl terminated polyether as described in U.S. Patent No. 5,094,667.

In another embodiment of the invention the polyetheramine is prepared by reacting the polyether intermediate derived from butylene oxide with an amine in an amination reaction to give an aminated polyether as described in European Publication No. EP310875. The amine can be a primary or secondary monoamine, a polyamine containing an amino group with a reactive N-H bond, or ammonia.

The high molecular weight polyetheramine of the present invention can have a number average molecular weight of 300 or 350 to 5000, in another instance of 400 to 3500, and in further instances of 450 to 2500 and 1000 to 2000.

In another embodiment of the invention the high molecular weight polyetheramine of the present invention can be represented by the formula $R(OCH_2CHR^1)_xA$ where R is a C_6 to C_{30} alkyl group or a C_6 to C_{30} alkyl-substituted phenyl group; R^1 is ethyl; x is a number from 5 to 50; and A is $OCH_2CH_2CH_2NH_2$ or $-NR^2R^3$ wherein R^2 and R^3 are independently hydrogen, a hydrocarbyl group, or $-(R^4NR^5)_yR^6$ wherein R^4 is an alkylene group having 2 to 10 carbon atoms, R^5 and R^6 are independently hydrogen or a hydrocarbyl group, and y is a number from 1 to 7. Throughout this application an alkylene group is a divalent alkane group. In a further embodiment of the polyetheramine of the invention, R is a C_8 to C_{24} alkyl group, x is a number from 15 to 30, and A is $-OCH_2CH_2CH_2NH_2$.

The detergent composition of this invention can be (E) a mixture of detergent compositions (A), (B), (C) and (D). In an embodiment of the invention the mixture (E) includes two or more components taken from a single detergent composition type such as a mixture of two components taken from detergent composition (A). In another

embodiment of this invention the mixture (E) includes one or more components taken from a detergent type and one or more components taken from one or more of the other three detergent types such as a mixture of a component taken from detergent composition (B) and a component taken from detergent composition (D).

5 The method of the present invention improves the performance of a lubricating oil of an internal combustion engine. The lubricating oil comprises an oil of lubricating viscosity, which can be a natural oil, a synthetic oil, or mixtures thereof. Natural oils include various refined mineral oils, animal oils, and vegetable oils. Synthetic oils include hydrogenated poly(alpha-olefins), poly(alkylene glycol)s, and esters of carboxylic acids.

10 In an embodiment of the invention the lubricating oil can be an American Petroleum Institute Group I-V base oil or a mixture thereof. The lubricating oil of the present invention can further comprise one or more lubricating oil additives to include nitrogen-containing dispersants such as polyisobutenylsuccinimides, metal-containing detergents such as alkali and alkaline earth metal neutral and overbased salts of alkylaryl sulfonates,

15 antioxidants such as sulfurized olefins which can be sulfides or polysulfides or mixtures thereof, antiwear agents such as zinc dialkyl dithiophosphates and organic molybdenum compositions, corrosion inhibitors such as tolyltriazole, viscosity modifiers to include viscosity index improvers and pour point depressants such as various polyolefins and polymethacrylates, friction modifiers such as glycerol mono- and dioleate, and antifoam

20 agents such as silicones. Lubricating oil additives can be present in a lubricating oil and at a level to provide the required performance for an internal combustion engine. The level of the lubricating oil additive in the lubricating oil can range from about 0.1 ppm by weight to about 20% by weight.

 In the method of the present invention a detergent composition can be introduced

25 into a combustion chamber of an internal combustion engine as a component of a fuel composition. The fuel composition comprises a normally liquid fuel. The normally liquid fuel can include a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel can be a petroleum distillate to include a gasoline as defined by ASTM specification D4814 or a diesel fuel as defined by ASTM specification D975. The

30 nonhydrocarbon fuel can be an oxygen-containing composition to include an alcohol, an ether, a nitroalkane, an ester of a vegetable oil, or a mixture thereof. Useful nonhydrocarbon fuels include methanol, ethanol, diethyl ether, methyl t-butyl ether,

nitromethane, and methyl esters of vegetable oils such as the methyl ester of rapeseed oil. Useful mixtures of a hydrocarbon and nonhydrocarbon fuel include a mixture of gasoline and ethanol and a mixture of a diesel fuel and a biodiesel fuel such as the methyl ester of rapeseed oil. In an embodiment of the invention the fuel composition comprises an emulsified water in oil composition that contains the normally liquid fuel as described above which can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. This emulsified water in oil composition can be prepared by a mechanical mixing, by including one or more emulsifiers and/or surfactants in the composition, or by a combination of mechanical mixing and inclusion of emulsifiers and/or surfactants.

10 The fuel composition of the present invention can further comprise one or more fuel additives to include nitrogen-containing detergents, amine-containing polyethers, metal-containing detergents, antioxidants such as hindered phenols, rust inhibitors such as alkenylsuccinic acids, corrosion inhibitors, combustion improvers such as nitroalkanes, demulsifiers, antifoaming agents, valve seat recession additives, metal deactivators, 15 lubricity agents, bacteriostatic agents, gum inhibitors, anti-icing agents, anti-static agents, organometallic fuel-borne catalysts for improved combustion performance, low temperature flow improvers, and fluidizers such as mineral oils, polyolefins and polyethers.

 In an embodiment of the invention the fuel additive can be a partial ester having at least one free hydroxyl group and formed by reacting at least one fatty carboxylic acid or reactive equivalent thereof, such as an anhydride or an ester or an acid halide, and a polyol. The fatty carboxylic acid can have 4 to 40 carbon atoms and in other instances 8 to 26 and 12 to 24 carbon atoms. The fatty carboxylic acid can be a monocarboxylic acid or polycarboxylic acid or a mixture thereof; can have a straight chain or branched chain or 25 be a mixture thereof; and can be saturated or unsaturated or a mixture thereof. Saturated and unsaturated mono- and dicarboxylic acids are useful and include capric, lauric, myristic, palmitic, stearic, behenic, oleic, petroselinic, elaidic, palmitoleic, linoleic, linolenic, erucic, and octadecenylsuccinic acid. The polyol can have two or more hydroxyl groups. Polyols useful in this invention include alkylene glycols, polyalkylene glycols, diols, triols and polyols having four or more hydroxyl groups. Examples of useful 30 polyols are ethylene glycol, neopentyl glycol, diethylene glycol, glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol, and sorbitol. Partial esters of the

present invention are commercially available or can be prepared by reacting a fatty carboxylic acid or reactive equivalent thereof and a polyol by methods well known in the art. The partial esters can be prepared from a fatty carboxylic acid and a polyol or from mixtures thereof. In another embodiment of the invention two or more partial esters are prepared separately from one another and then mixed. An example of a useful partial ester is a mixture of glycerol monooleate and glycerol dioleate.

In another embodiment of the invention the fuel additive can be an amine-containing polyether. The amine-containing polyether can contain two or more ether units and is generally prepared from a polyether intermediate. The polyether intermediate can be the reaction product of one unit of a hydroxy-containing hydrocarbyl compound and two or more units of a) an alkylene oxide other than butylene oxide or b) two or more different alkylene oxides that can include butylene oxide. The hydroxy-containing hydrocarbyl compound can be an alcohol or an alkyl-substituted phenol where the alcohol or alkyl substituent of the phenol can have 1 to 50 carbon atoms, 6 to 30 carbon atoms in a second instance, and 8 to 24 carbon atoms in a third instance. The alcohol or alkyl substituent of the phenol can have a straight carbon chain, branched carbon chain, or a mixture thereof. The alkylene oxide can have 2 to 18 carbon atoms, 2 to 12 carbon atoms in another instance, and 2 to 8 carbon atoms in a further instance. Two or more different alkylene oxides can be reacted with the hydroxy-containing hydrocarbyl compound as a mixture or in a sequential fashion to form the polyether intermediate. The polyether intermediate can have 2 to 100 repeating alkylene oxide units, in another embodiment 5 to 50 alkylene oxide units, and in an additional embodiment 15 to 30 alkylene oxide units. U.S. Patent No. 5,094,667 provides reaction conditions for preparing the polyether intermediate. The amine-containing polyether can include a reaction product of a) the polyether intermediate derived from an alkylene oxide or two or more different alkylene oxides and b) an amine to include ammonia, a primary or secondary monoamine, or a polyamine. The amine-containing polyether can include a reaction product of a) the polyether intermediate from one or more alkylene oxides and b) acrylonitrile to form a nitrile product that is hydrogenated to form an aminopropyl terminated polyether. The amine-containing polyether can include a reaction product of a) the above described aminopropyl terminated polyether derived from one or more alkylene oxides and b) an aldehyde such as formaldehyde to form a product that can include a heterocycle that is a

N-substituted perhydro-S-triazine as described in U.S. Patent No. 5,830,243. This reaction product of an aminopropyl terminated polyether and an aldehyde can also be prepared from an aminopropyl terminated polyether derived from a polyether intermediate that is prepared from butylene oxide. The amine-containing polyether can include a reaction product of a) the polyether intermediate from one or more alkylene oxides and b) a carbonylating reagent such as phosgene to form in the case of phosgene a chloroformate ester that is then reacted with a polyamine to form a polyether-containing, amine-containing carbamate as described in U.S. Patent No. 5,503,644. The polyether-containing, amine-containing carbamate can also be prepared from a polyether intermediate that is prepared from butylene oxide.

In an additional embodiment of the invention the fuel additive can be a polyether. The polyether can contain two or more ether units. The polyether can be prepared from the reaction of a hydroxy-containing hydrocarbyl compound and an alkylene oxide or two or more different alkylene oxides. The hydroxy-containing hydrocarbyl compound can be an alcohol or an alkyl-substituted phenol where the alcohol or alkyl substituent of the phenol can have 1 to 50 carbon atoms, 6 to 30 carbon atoms in a second instance, and 8 to 24 carbon atoms in a third instance. The alcohol or alkyl substituent of the phenol can have a straight carbon chain, branched carbon chain, or a mixture thereof. The alkylene oxide can have 2 to 18 carbon atoms, 2 to 12 carbon atoms in another instance, and 2 to 8 carbon atoms in a further instance. Useful alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, and mixtures thereof. Two or more different alkylene oxides can be reacted with the hydroxy-containing hydrocarbyl compound as a mixture or in a sequential fashion to form the polyether. The polyether can have 2 to 100 repeating alkylene oxide units, in another embodiment 5 to 50 alkylene oxide units, and in an additional embodiment 15 to 30 alkylene oxide units. U.S. Patent No. 5,094,667 provides reaction conditions for preparing the polyether.

The fuel composition can also include the nitrogen-containing detergent composition comprising (A), (B), (C), (D) or (E) as described above. The nitrogen-containing detergent composition can be present in the fuel composition at 10 to 20,000 ppm by weight and in other instances at 0.1 to 10,000 and 50 to 2000 and 75 to 1200 and 100 to 900 ppm by weight. The nitrogen-containing detergent composition can be introduced into the fuel composition alone or in combination with one or more of the

above described fuel additives as a bulk treatment at a refinery or storage terminal, as an aftermarket treatment for example by addition to a fuel in a fuel storage tank of a motorized vehicle, or via a dosing system into a fuel system of an internal combustion engine. Alternatively the nitrogen-containing detergent composition alone or in combination with one or more of the above described fuel additives can be introduced from a dosing system directly into a combustion chamber of an internal combustion engine at a rate that is equivalent to the treatment levels of the detergent composition and fuel additives used in the fuel composition. In an embodiment of the invention the detergent composition further comprises a fuel additive or a mixture of fuel additives as described hereinabove. In another embodiment of the invention the detergent composition comprises a combination of a hydroxyalkyl-substituted fatty amine represented by the formula $RN[(A^1O)_xH][(A^2O)_yH]$ as described above for detergent composition (B) and a partial ester of a fatty carboxylic acid and a polyol where the ester has at least one free hydroxyl group as described above for fuel additives that can be present in a fuel composition. The combination of the partial ester and the hydroxyalkyl-substituted fatty amine can be in a weight ratio of respectively 0.25-1:0.25-1 and in other instances of 0.5-1:0.5-1 and 0.75-1: 0.75-1 and 1:1.

The above described fuel additives can be included in the fuel composition of the present invention for fuel and lubricating oil performance requirements depending on the type of internal combustion engine and the characteristics of the fuel being used. In general the fuel additives can be used in the fuel composition at 10 to 20,000 ppm by weight and in other instances at 0.1 to 10,000 and 0.3 to 1000 and 0.5 to 700 ppm by weight.

Detergent compositions and fuel compositions of the present invention containing two or more components can generally be prepared by admixing the components. Their preparation can include the use of hydrocarbon solvents, mineral oils and synthetic base oils to facilitate the admixing, and mixing via a mechanical means at room or elevated temperatures can also be employed.

Both recent and future lubricating oil performance requirements and exhaust emission requirements for internal combustion engines are placing additional performance demands on the lubricating oil. The method of the present invention provides a way to improve performance of the lubricating oil by meeting these additional performance

demands. These lubricating oil performance requirements and exhaust emission requirements for internal combustion engines include a) extended intervals between lubricating oil changes or drains, b) internal combustion engines containing an exhaust gas recirculation system, c) internal combustion engines having an exhaust treatment device and run on a low sulfur content fuel, d) internal combustion engines having an exhaust treatment device and a lubricating oil that has a reduced level of sulfur, phosphorus and/or sulfated ash where sulfated ash is a measure of the metal content in the oil, and e) various combinations thereof. Exhaust treatment devices can include three-way catalytic converters, NO_x traps, oxidation catalysts, reduction catalysts and diesel particulate filters.

10 In an embodiment of the method of the present invention the internal combustion engine is a compression-ignited engine having an exhaust gas recirculation system. In an additional embodiment of the method of the invention the internal combustion engine is a spark-ignited direct injection engine having an exhaust gas recirculation system. In another embodiment of the method of the invention the engine is a spark-ignited or compression-

15 ignited engine having an exhaust treatment device, and the lubricating oil has at least one of the properties selected from the group consisting of a phosphorus content below 0.1% by weight, a sulfur content below 0.5% by weight, and a sulfated ash content below 1.5% by weight. In other instances the phosphorus content of the lubricating oil can be below 0.08 or 0.05% by weight, the sulfur content of the lubricating oil can be below 0.3 or 0.2%

20 by weight, and the sulfated ash content of the lubricating oil can be below 1.2 or 1% by weight. In still other instances the phosphorus content of the lubricating oil can be 0.02 to 0.06% by weight, the sulfur content of the lubricating oil can be 0.1 to 0.4% by weight, and the sulfated ash content of the lubricating oil can be 0.1 to 0.9% by weight. In a further embodiment of the method of the present invention the engine is a spark-ignited or

25 compression-ignited engine having an exhaust treatment device, and a fuel of a fuel composition has a sulfur content below 80 ppm by weight. In other instances the sulfur content of the fuel can be below 50, 15 or 10 ppm by weight. In still a further embodiment of the method of the invention an engine is installed in a motor vehicle and has a recommended drain interval for a lubricating oil of the engine of greater than 6,000 miles

30 and in other instances of greater than 8,000 or 10,000 miles. In another embodiment of the method of the present invention a stationary engine has a recommended drain interval for

a lubricating oil of the engine of greater than 150 operational hours and in other instances of greater than 200 or 250 operational hours.

The following examples demonstrate the method of the present invention where the introduction of the detergent composition into a combustion chamber of an internal combustion engine results in improvement in the performance of a lubricating oil of the engine. The examples are provided for illustrative purposes only and are not intended to limit the scope of the invention.

VW Fleet Trial

A fleet of six, identical vehicles was used to investigate fuel additive and lubricant interactions. The vehicles were model year 2000 Volkswagen Passats equipped with 1.9L turbo, direct injection engines. This modern engine design is equipped with exhaust gas recirculation (EGR) and meets Euro 3 emissions standards. Fuel is injected through high-pressure unit injectors directly into the combustion chamber.

The test program involved two separate phases, each operated for 50,000 kilometers. Mileage accumulation followed a driving cycle that included urban, suburban and motorway conditions. During each phase of the test, vehicles were assigned to a specific combination of fuel and lubricant as outlined in Table 1. The test fuels varied by additive including; no additive, additive of Example A, and additive of Example B. Example A was the reaction product of a polyisobutenylsuccinic anhydride derived from 1000 molecular wt. high vinylidene polyisobutylene and tetraethylenepentamine in a mole ratio of 1:0.87. Example B was the reaction product of an alkylphenol derived from 1000 molecular wt. high vinylidene polyisobutylene, 37 wt.% aqueous formaldehyde and ethylenediamine in a mole ratio of 1:1.15:1.1. Diesel fuel A was procured from a commercial source in the United Kingdom. The fuel did not contain dispersant/detergent additives and met the EN590 specifications. Analysis of the fuel is shown in Table 2.

Table 1: Test Matrix Design

Vehicle	Phase 1		Phase 2	
	Oil	Fuel Additive	Oil	Fuel Additive
1	0W-30	None	0W30	Example A
2	5W-40	None	5W40	Example B
3	0W-30	Example A	0W30	Example B
4	5W-40	Example A	5W40	None
5	0W-30	Example B	0W30	None
6	5W-40	Example B	5W40	Example A

Table 2: Test Fuel Properties

Property	Result
	Fuel A
Specific Gravity @ 15 °C	0.8399
T95	334 °C
Final Boiling Pint	349 °C
Cetane Number	49.3
Sulfur Content	34 ppm mass
Water Content	72 ppm
Oxidation Stability	0.2mg/100 ml
Lubricity by HFRR (wear scar diameter)	277 μ m
Olefins	2 volume %

5 Two different lubricant formulations were used during the test program: a 0W-30, fully synthetic lubricating oil having 0.1040 %wt P, 0.53%wt S, TBN = 11.0, TAN= 2.8, and 1.61 % sulfated ash; and a 5W-40 partially synthetic oil having 0.085%wt P, 0.4600%wt S, TBN = 9.3, TAN = 2.8, and 1.24%wt sulfated ash.

10 During each phase of testing, the crankcase was filled only once. Interim samples were taken from each vehicle every 10,000 kilometers for used oil analysis. Each group of three vehicles using a particular lubricant was treated as a set. For each set of vehicles the interim samples were removed from the crankcase, then the amount of "top up" oil needed for each vehicle was calculated. The vehicle needing the most "top up" oil was treated as the baseline and some lubricant was removed from the other two vehicles in the set to

achieve the same crankcase level. Then all three vehicles were given the same amount of "top up" oil. In this manner, all vehicles operating on the same lubricant always received the same amount of additional oil and the crankcase oil of all three vehicles aged at the same rate.

5 Plots of the TBN (total base number in mg equivalents of KOH per gram of sample) and percent change in TBN for the end of test (EOT) used 0W30 and 5W40 oil samples are provided in Figures 1 and 2. Used oil samples from vehicles using a fuel that contained a dispersant/detergent showed higher end of test TBN levels compared to vehicles using a fuel that contained no dispersant/detergent indicating that the oil for
10 vehicles using a fuel containing dispersants/detergents retained more TBN compared to the start of test TBN. The amount of TBN remaining in engine oil is a measure of the effectiveness of the lubricating oil to protect the engine from the acidic materials, such as soot, generated by the incomplete combustion of fuel. The higher the TBN of the oil at
15 end of test, the better the oil is performing. Figures 1 and 2 indicate a significant improvement for those oils coming from engines operated on fuels comprising dispersants/detergents.

 Plots of the average piston ratings for the engines from the ends of each phase are provided in Figure 3. Engines operated on fuels comprising a dispersant/detergent showed cleaner pistons. Engine cleanliness is a direct measure of the effectiveness of a lubricating
20 oil to protect key engine parts such as the piston. Figure 3 indicates that the performance of the lubricant oils in those engines operated on fuels comprising a dispersant or detergent were significantly enhanced.

 Engine out and tail pipe emissions were measured using both the ECE and the EUDC driving cycle. Emission measurements were obtained at three points during each
25 test phase. The first emissions test points were taken at the start of test with fresh lubricant in the crankcase. The second emissions test points were taken after the mileage accumulation with the used lubricant. Finally, the third emissions test points for each phase were taken after the mileage accumulation with a fresh charge of lubricant in the crankcase. This test design gives the ability to determine the different effects that occur
30 during mileage accumulation, making it possible to separate the effect of used lubricant on emissions and the effect of the engine deposits on emissions. Plots of the particulate emissions for the two driving cycles are provided in Figure 4. As indicated by Figure 4,

the particulate emissions for vehicles using a fuel containing the dispersant/detergent of Example A were significantly lower in both emissions driving cycles.

Ford Crown Victoria Fleet Trial

Four vehicles were used to investigate fuel additive and lubricant interactions. The vehicles were 1991-1992 Ford Crown Victorias equipped with 4.6L engines and automatic transmissions. The test program consisted of evaluating two fuels, one baseline fuel with no additive, and the same baseline fuel additized with a combination of dispersants/detergents of Examples C and D. Example C was the reaction product of a chlorinated 1300 molecular wt. polyisobutylene, ethylenediamine and sodium hydroxide. Example D was a polyetheramine prepared by reacting a C₁₂₋₁₅ alcohol with an average of 24 units of propylene oxide, reacting the propoxylated alcohol with acrylonitrile to form a nitrile and hydrogenating the nitrile. Mileage accumulation followed a driving cycle that consisted of 70% highway driving and 30% city driving. Two vehicles, one on base fuel and one on additized fuel, were driven for 30,000 miles. Intermediate inspection and oil change were done at 15,000 miles and at end of test (30,000 miles). The remaining two vehicles, one on base fuel and one on additized fuel, were run for 15,000 miles with only a final inspection at the end of test. All four vehicles were run using a 5W-30 lubricating oil meeting the SG American Petroleum Institute automotive gasoline engine service category. The performance of the two fuels were comparatively evaluated by used oil analysis, especially TBN retention.

Plots of the TBN for used oil samples at 15,000 miles and 30,000 miles are provided in Figure 5. Used oil samples from vehicles using dispersant/detergent showed higher end of test TBN levels compared to vehicles using no dispersant/detergent, indicating that the oil for vehicles using a fuel that contained dispersants/detergents retained more of its original TBN. The amount of TBN remaining in engine oil is a measure of the effectiveness of the lubricating oil to protect the engine from the acidic materials generated from the combustion of fuel. The higher the TBN of the used oil, the better the oil is performing. Figure 5 indicates a significant improvement for those oils coming from engines operated on fuels comprising dispersants/detergents.

Ford Direct Injection Fleet Trial

Three identical vehicles were used to investigate fuel additive and lubricant interactions. The vehicles were Ford pre-production 3 cylinder direct injection spark ignited 1.125L engines equipped with EGR.

- 5 The test program, as outlined in Table 3, involved operating each vehicle for 30,000 km. Mileage accumulation followed a driving cycle that included urban, suburban, and motorway conditions. The vehicles were assigned to specific combinations of fuel and lubricant as outlined in Table 3. The test fuel varied by additive including: no additive and additive of Example B which was a Mannich reaction product as described above for
10 the VW fleet trial. The fuel was procured from a commercial source in the United Kingdom. The fuel did not contain dispersant/detergent additives except for those added in the study.

Table 3

Vehicle	Oil	Fuel Additive
1	Normal Ash	None
2	Reduced Ash	None
3	Normal Ash	Example B

- 15 Two different lubricant formulations were used during the test program: a lubricating oil having Ford M2C913A approval and containing 1.2%wt sulfated ash; and a reduced ash (0.8%wt sulfated ash) lubricating oil capable of meeting ACEA A1/B1 criteria.

- 20 Plots of the TBN for the used oil samples are provided in Figure 6. Used oil samples from vehicle 2 containing the reduced ash lubricating oil showed an earlier TBN:TAN (total acid number in mg equivalents KOH per gram of sample) cross-over (10,000 km) than the used oil samples from vehicle 1 containing the normal ash lubricating oil (14,000 km). The TBN:TAN cross-over is an indication of the effectiveness of the lubricating oil to protect the engine from the acidic by-products of the
25 combustion process. The higher the distance accumulated before TBN:TAN cross-over, the better the oil is performing. As Figure 6 indicates, the addition of a dispersant/detergent to the fuel in vehicle 3 increased the distance accumulated prior to TBN:TAN cross-over from 14,000 km of vehicle 1 to 18,000 km.

Liebherr 914T Engine Test

Emissions data for a base fuel and base fuel plus a mixture of dispersant/detergent were obtained on a Liebherr 914T engine using 4 points of the ISO8178 off-road test cycle. These data points vary in the speed and load conditions that the engine is run at.

5 Plots of the total particulate emissions for the base fuel and the base fuel containing an additive package comprising the three dispersants/detergents of Examples E, F and G are provided in Figure 7. Example E was the reaction product of hexadecenylsuccinic anhydride and diethylethanolamine in a mole ratio of 1:1.35. Example F was the reaction product of a 60 wt.% and 40 wt.% mixture of polyisobutenylsuccinic anhydrides derived from respectively 2300 and 1000 molecular wt. high vinylidene polyisobutylene, ethylene glycol, and dimethylaminoethanol. Example G was the reaction product of a polyisobutenylsuccinic anhydride derived from a 2300 molecular wt. high vinylidene polyisobutylene and heavy polyethylenepolyamines. Plots of the particulate emissions in the 20-200 nm size spectrum for the base fuel and the base fuel containing an additive

10 package comprising the three dispersants/detergents of Example E, F and G are provided in Figure 8. Surprisingly, both plots of Figures 7 and 8 indicate that the use of the dispersant/detergent can lower the particulate emissions of an internal combustion engine. Of significant importance, Figure 8 indicates that the use of the dispersant/detergent lowers the ultra fine particulates by 8%.

20 M-B M111E Engine Test

A baseline fuel (no additive) and the same fuel additized with dispersant /detergent of Example B, the Mannich reaction product described above in the VW fleet trial, were evaluated in the Mercedes-Benz or M-B M111E (Test Method CEC-L-53-T-95) engine test. This engine test is part of the ACEA A1, A2, and A3 test specifications. The test

25 evaluates engine sludge and cam wear performance of a lubricating oil. Each fuel, baseline and additized, was evaluated in the M111E engine test at two independent testing facilities. The sludge ratings for the baseline fuel and the additized fuel are provided in Figure 9. As the data indicates, significant improvements in the sludge rating of the M111E engine test were achieved with the fuel additized with dispersant of Example B

30 versus the non-additized baseline fuel.

ASTM Sequence VE Engine Test

TABLE 4

ASTM Sequence VE Engine Wear ¹			
Example	Fuel Treatment	Max Cam Lobe Wear, micrometers	Iron in oil, ppm ⁶
H	None	192	717
I	600 ppm PEA-1 ²	95	407
J	420 ppm PIBEDA +282 ppm PEA-2 ³	161	788
K	600 ppm [PEA-2/formaldehyde] ⁴	273	1219
L	600 ppm PEA carbamate ⁵	262	801

¹ ASTM Sequence VE engine test was run using a Phillips J unleaded reference fuel and the Reference Oil #1002, a GF-2 ILSAC service category gasoline engine oil.

5 ² PEA-1 is a polyetheramine prepared by reacting C₁₃ alcohol with butylene oxide in respectively a 1:20 mole ratio to form a polyether, condensing the polyether with acrylonitrile to form a nitrile, and hydrogenating the nitrile to form the polyetheramine.

10 ³ PIBEDA contains as 65% by weight actives the reaction product of a chlorinated 1300 molecular weight polyisobutylene reacted with ethylenediamine; PEA-2 is an amine-containing polyether prepared as described above for PEA-1 except that the polyether is prepared by reacting C₁₂₋₁₅ alcohol and propylene oxide in respectively a 1:24 mole ratio.

⁴ [PEA-2/formaldehyde] is the reaction product of the amine-containing polyether PEA-2 described above reacted with formaldehyde in a 1:1 mole ratio.

15 ⁵ PEA carbamate is a polyether-containing, amine-containing carbamate derived from (a) the polyether prepared by reacting dodecylphenol and butylene oxide in respectively a 1:20 mole ratio and (b) a polyethylenepolyamine.

⁶ The amount of iron metal in the oil at the end of test after 288 hours.

20

25

30

Ford Crown Victoria Engine Test

TABLE 5

1992/1994 Ford 4.6l Crown Victoria Vehicle Engine Wear ¹		
Example	Fuel Treatment	Iron in oil, ppm ⁶
M	None	86
N	700 ppm [PEA-2/formaldehyde] ²	168
O	400 ppm Mannich +312 ppm PEA-2 ³	65
P	125 ppm ETA + 125 ppmGMO ⁴	49
Q	360 ppm PEA-1 +190 ppm PE-1 ⁵	53

¹ 1992/1994 Ford 4.6l Crown Victoria vehicle engine test was run over 7,500 miles using an unleaded regular fuel and a 10W-30 SH oil.

5 ² [PEA-2/formaldehyde] is the same as the [PEA-2/formaldehyde] reaction product described above in Table 1.

10 ³ The Mannich is 65% by weight actives of the reaction product prepared by reacting 1000 molecular weight polyisobutylene alkylated phenol, formaldehyde and ethylenediamine; PEA-2 is the same as the PEA-2 amine-containing polyether described above in Table 1.

⁴ ETA is a diethoxylated tallowamine; GMO is glycerol monooleate.

⁵ PEA-1 is the same as the PEA-1 polyetheramine described above in Table 1; PE-1 is a polyether formed by reacting C₁₃ alcohol and butylene oxide in respectively a 1:20 mole ratio.

15 ⁶ Iron wear metal in the oil as an average of the top and bottom drain.

Each of the documents referred to in this Detailed Description of the Invention section is incorporated herein by reference. All numerical quantities in this application used to describe or claim the present invention are understood to be modified by the word "about" except for the examples or where explicitly indicated otherwise. All chemical
20 treatments or contents throughout this application regarding the present invention are understood to be as actives unless indicated otherwise even though solvents or diluents may be present.

What is claimed is:

- 5 1. A method of operating an internal combustion engine, comprising:
introducing a nitrogen-containing detergent composition comprising
- (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine;
 - (B) a hydrocarbyl-substituted amine;
 - (C) a Mannich reaction product of a hydrocarbyl-substituted hydroxy-containing
 - 10 aromatic compound, an aldehyde, and an amine;
 - (D) a high molecular weight polyetheramine prepared by reacting one unit of a hydroxy-containing hydrocarbyl compound with two or more units of butylene oxide to form a polyether intermediate, and aminating the polyether intermediate by reacting the polyether intermediate with an amine or with acrylonitrile and hydrogenating the reaction
 - 15 product of the polyether intermediate and acrylonitrile; or
 - (E) a mixture thereof into a combustion chamber of the engine during the operation of the engine wherein the detergent composition improves the performance of a lubricating oil of the engine.
- 20 2. The method of claim 1 wherein the detergent composition is introduced into the combustion chamber by injection from a dosing system or as a component of a fuel composition.
3. The method of claim 2 wherein the detergent composition is introduced into the combustion chamber as a component of the fuel composition wherein the detergent
- 25 composition improves the performance of the fuel composition.
4. The method of claim 1 wherein the detergent composition (A) is the reaction product of a polyisobutenylsuccinic acylating agent and a polyethylenepolyamine wherein the polyisobutenyl group has a number average molecular weight of 150 to 5000.
5. The method of claim 1 wherein the detergent composition (B) is derived from a
- 30 polyisobutylene having a number average molecular weight of 150 to 5000 and a polyamine.

6. The method of claim 1 wherein the Mannich reaction product is prepared from phenol alkylated with a polyisobutylene having a number average molecular weight of 120 to 3000, formaldehyde, and a secondary monoamine.
7. The method of claim 1 wherein the polyetheramine is represented by the formula
5 $R(\text{OCH}_2\text{CHR}^1)_x\text{A}$ wherein R is a C_6 to C_{30} alkyl group or a C_6 to C_{30} alkyl-substituted phenyl group; R^1 is ethyl; x is a number from 5 to 50; and A is $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or $-\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are independently hydrogen, a hydrocarbonyl group, or $-(\text{R}^4\text{NR}^5)_y\text{R}^6$ wherein R^4 is an alkylene group having 2 to 10 carbon atoms, R^5 and R^6 are independently hydrogen or a hydrocarbonyl group, and y is a number from 1 to 7.
- 10 8. The method of claim 1 wherein the detergent composition further comprises a fuel additive selected from the group comprising a nitrogen-containing detergent, an amine-containing polyether, a lubricity agent, a fluidizer, a metal-containing detergent, a rust inhibitor, a corrosion inhibitor, an antioxidant, a low temperature flow improver, a demulsifier, an antifoaming agent, a valve seat recession additive, a combustion improver,
15 a metal deactivator, or a mixture thereof.
9. The method of claim 8 wherein the detergent composition is a combination of a hydroxyalkyl-substituted fatty amine represented by the formula $\text{RN}[(\text{A}^1\text{O})_x\text{H}][(\text{A}^2\text{O})_y\text{H}]$ wherein R is a hydrocarbonyl group containing 4 to 30 carbon atoms, A^1 and A^2 are independently alkylene groups having 2 to 18 carbon atoms, and x and y are
20 independently zero or an integer where the sum of x and y is at least one; and a partial ester of a fatty carboxylic acid and a polyol wherein the ester has at least one free hydroxyl group.
10. The method of claim 1 wherein the engine is a compression-ignited engine or spark-ignited direct injection engine having an exhaust gas recirculation system.
- 25 11. The method of claim 1 wherein the engine is a spark-ignited or a compression-ignited engine having an exhaust treatment device, and the lubricating oil has at least one of the properties selected from the group consisting of a phosphorus content below 0.1% by weight, a sulfur content below 0.5% by weight, and a sulfated ash content below 1.5% by weight.

12. The method of claim 2 wherein the engine is a spark-ignited or a compression-ignited engine having an exhaust treatment device, and a fuel of the fuel composition has a sulfur content below 80 ppm by weight.

13. The method of claim 1 wherein the engine is installed in a motor vehicle and has a
5 recommended drain interval for the lubricating oil of the engine of greater than 6,000 miles.

14. The method of claim 1 wherein the engine is a stationary engine having a recommended drain interval for the lubricating oil of the engine of greater than 150 operational hours.

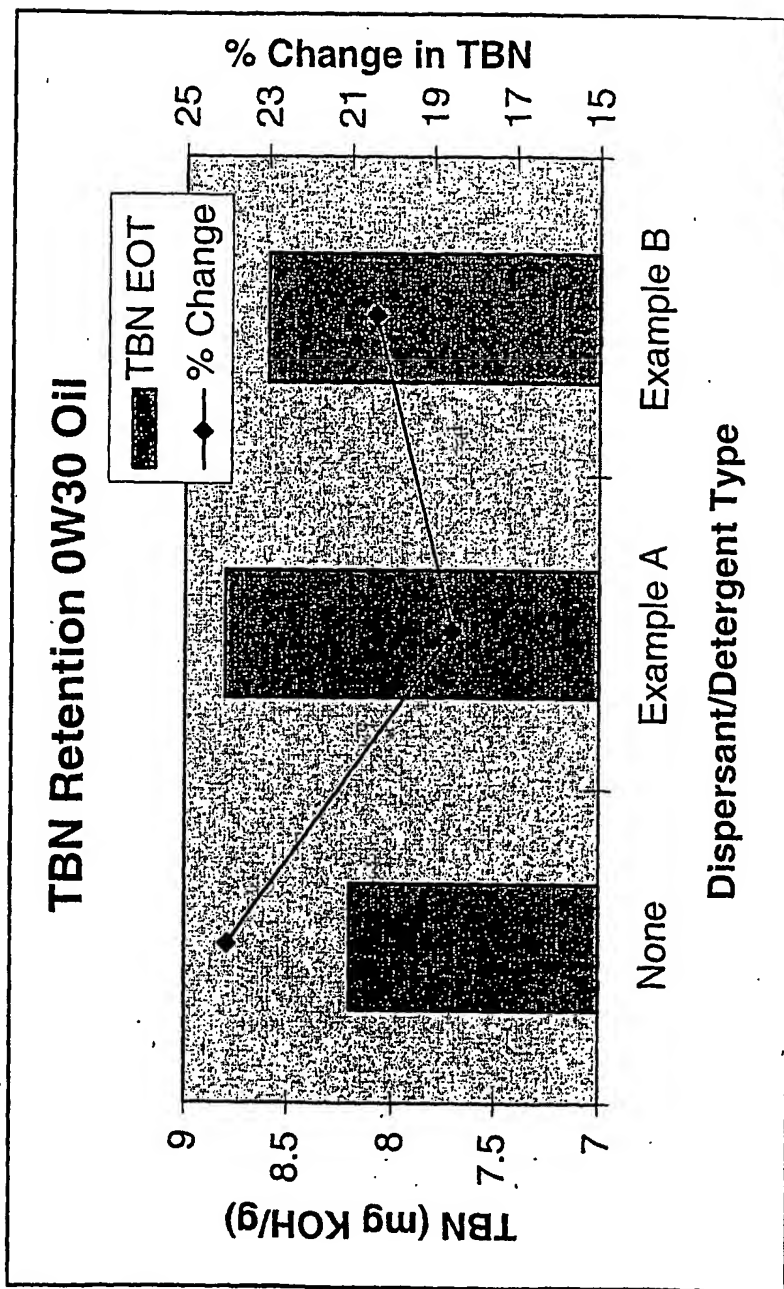


FIGURE 1

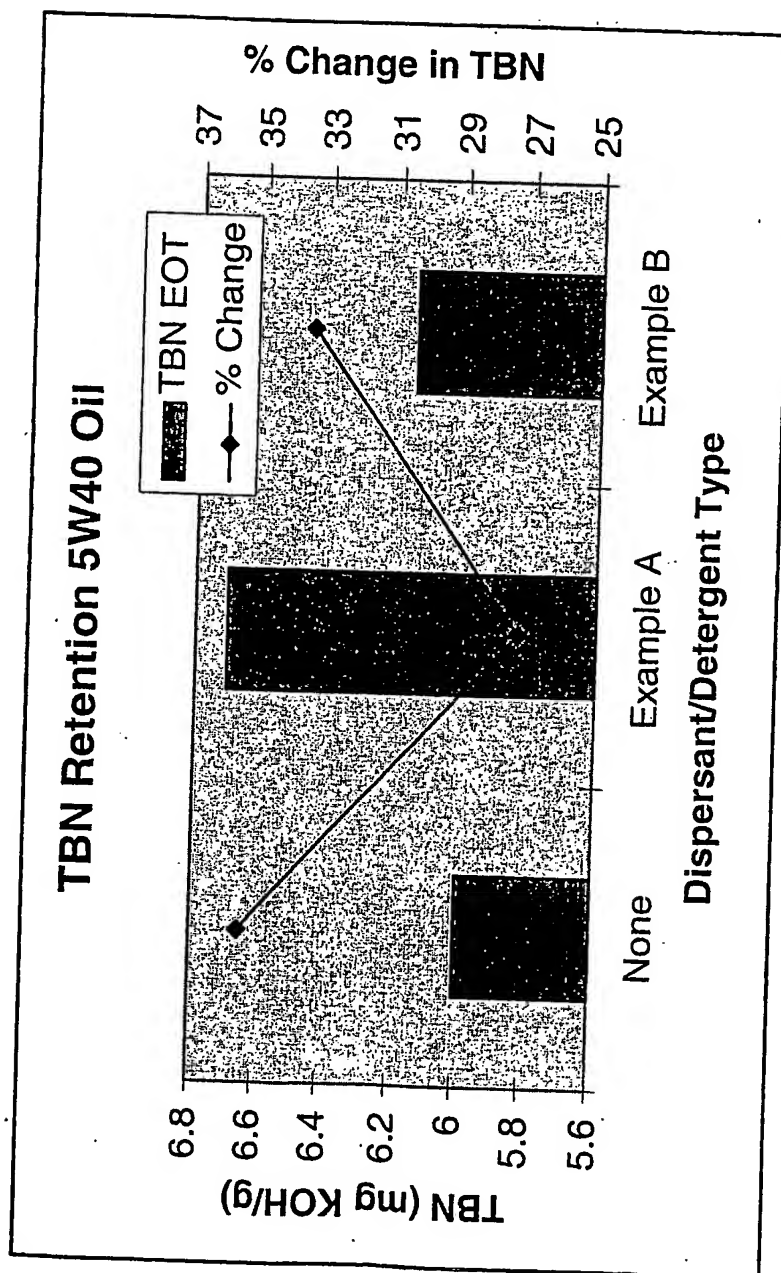


FIGURE 2

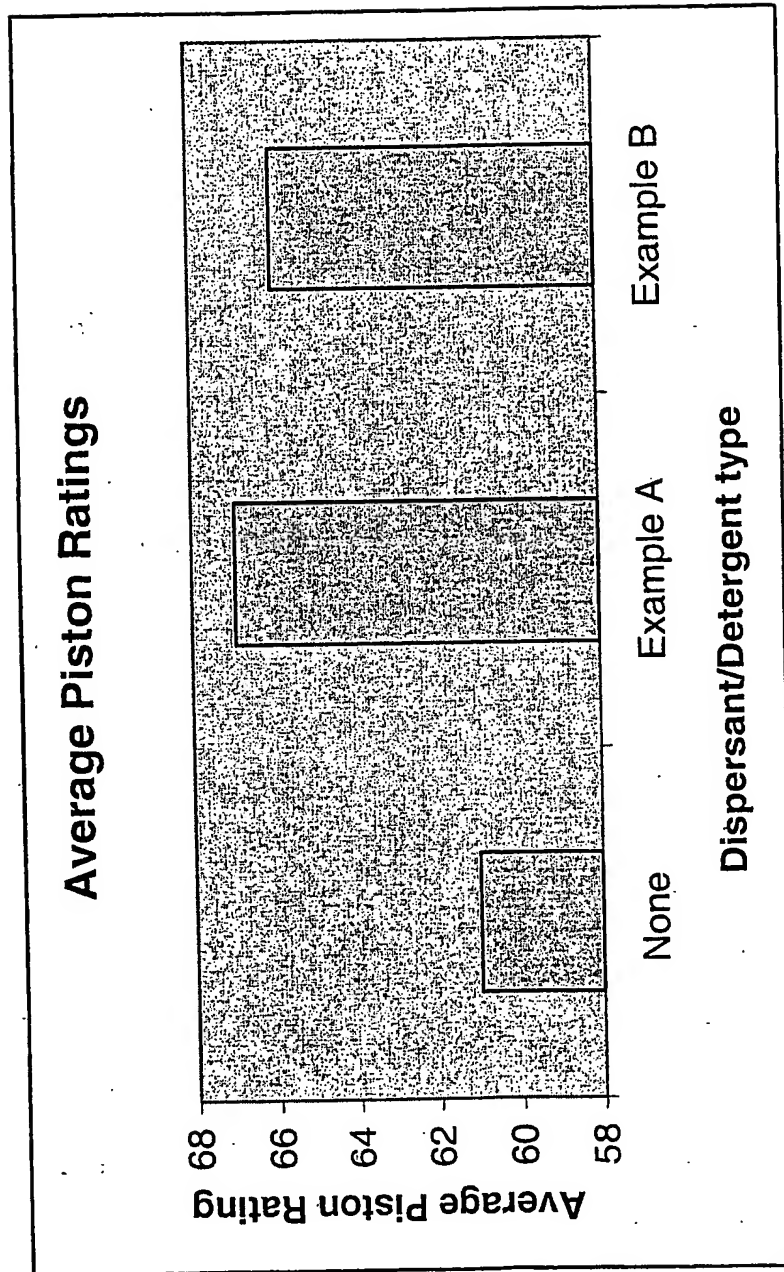


FIGURE 3

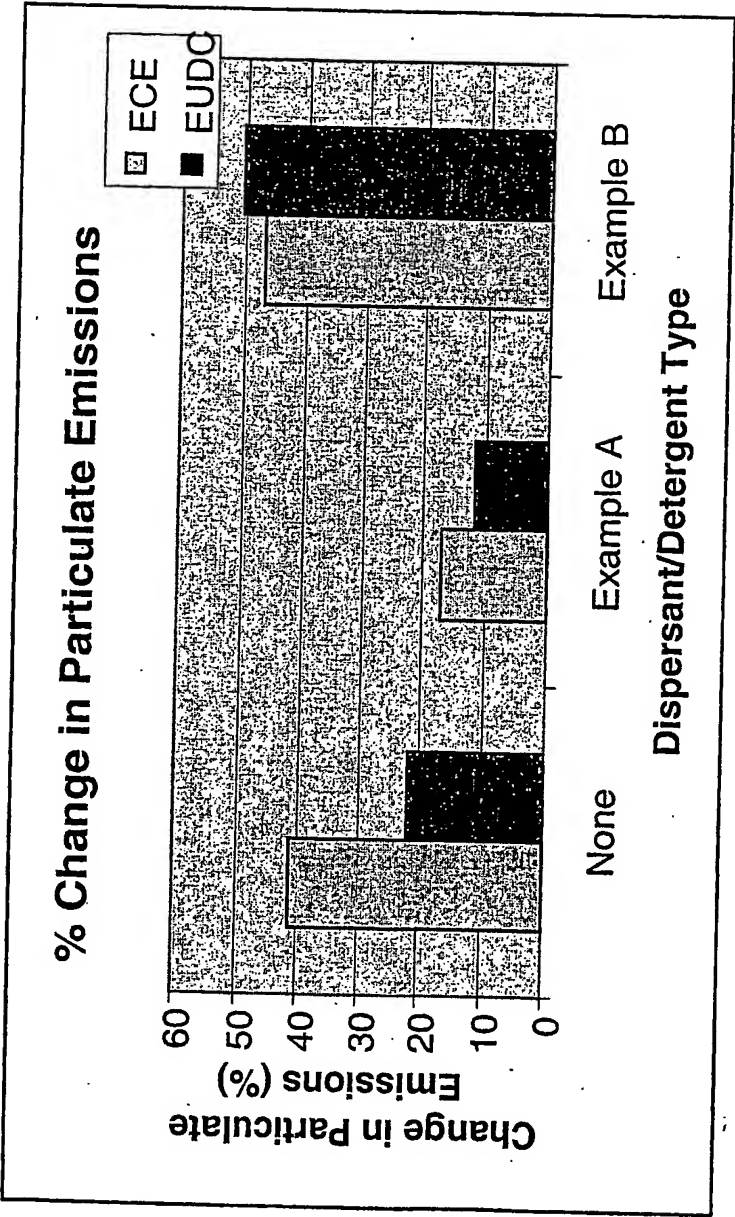


FIGURE 4

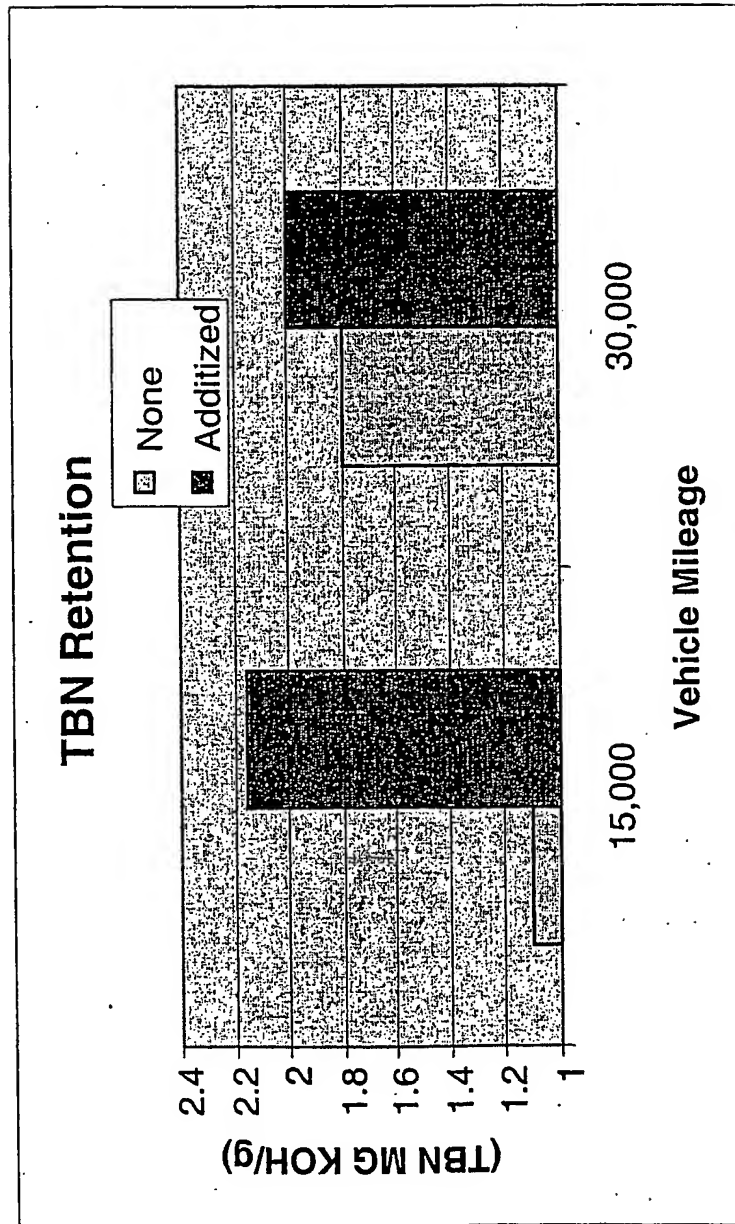


FIGURE 5

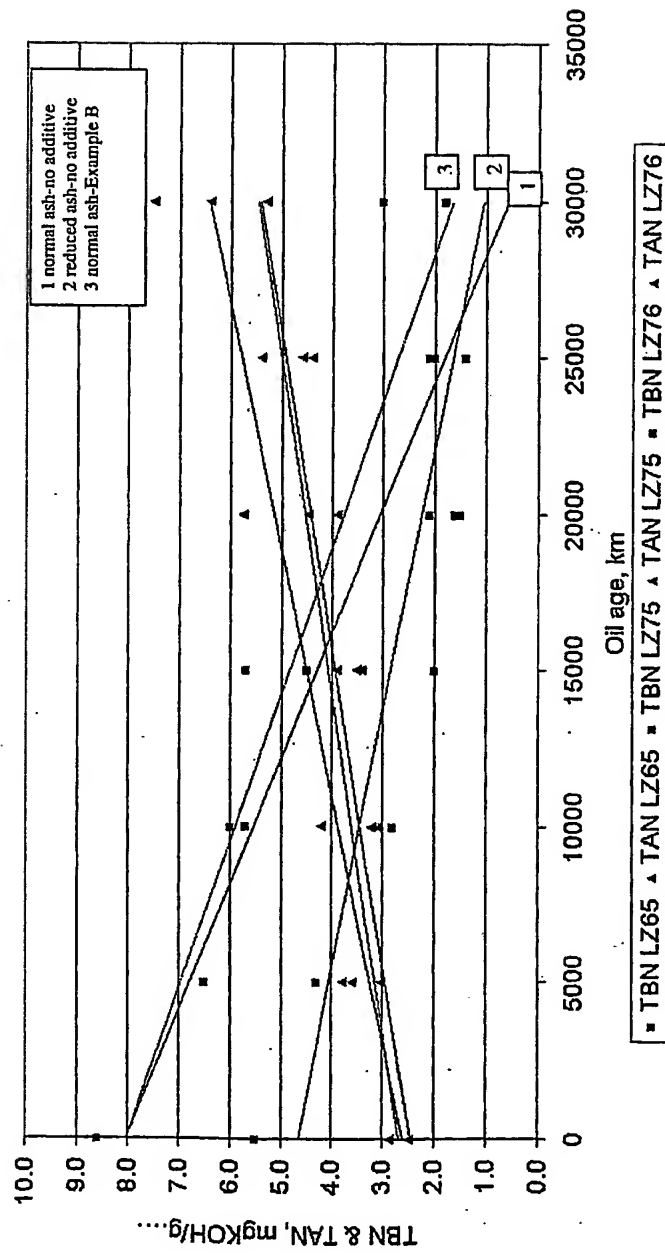


FIGURE 6

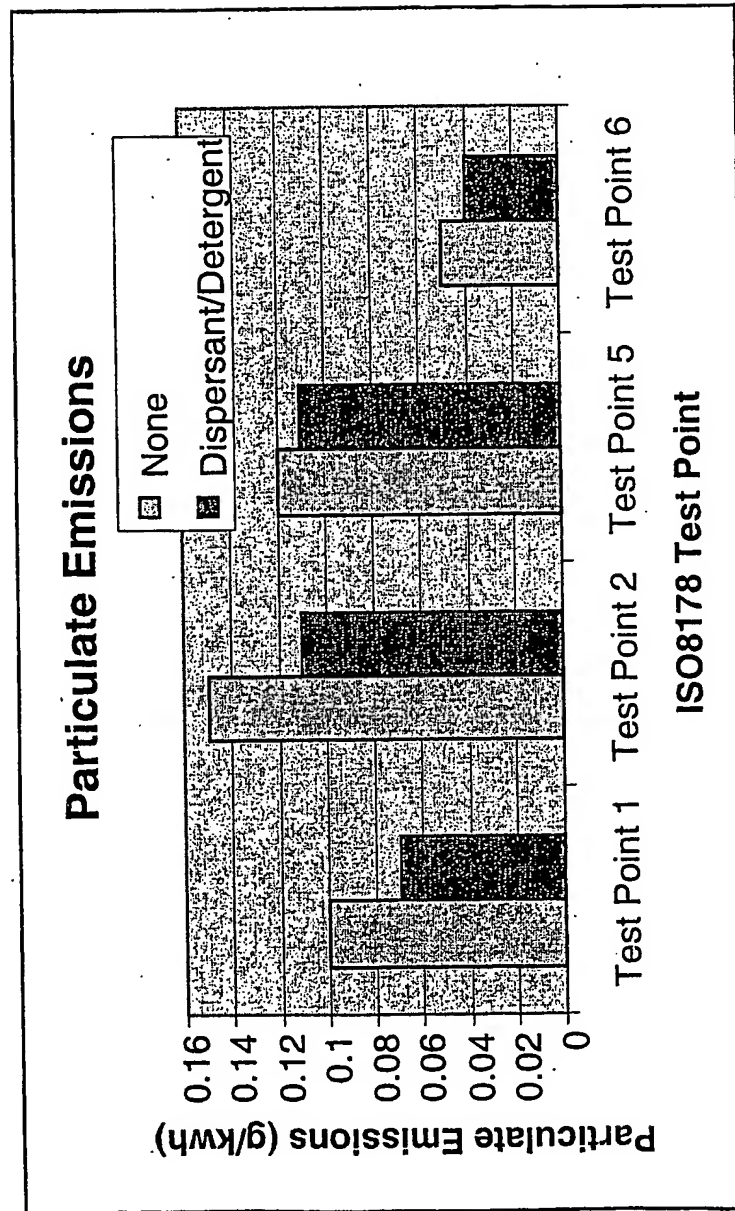


FIGURE 7

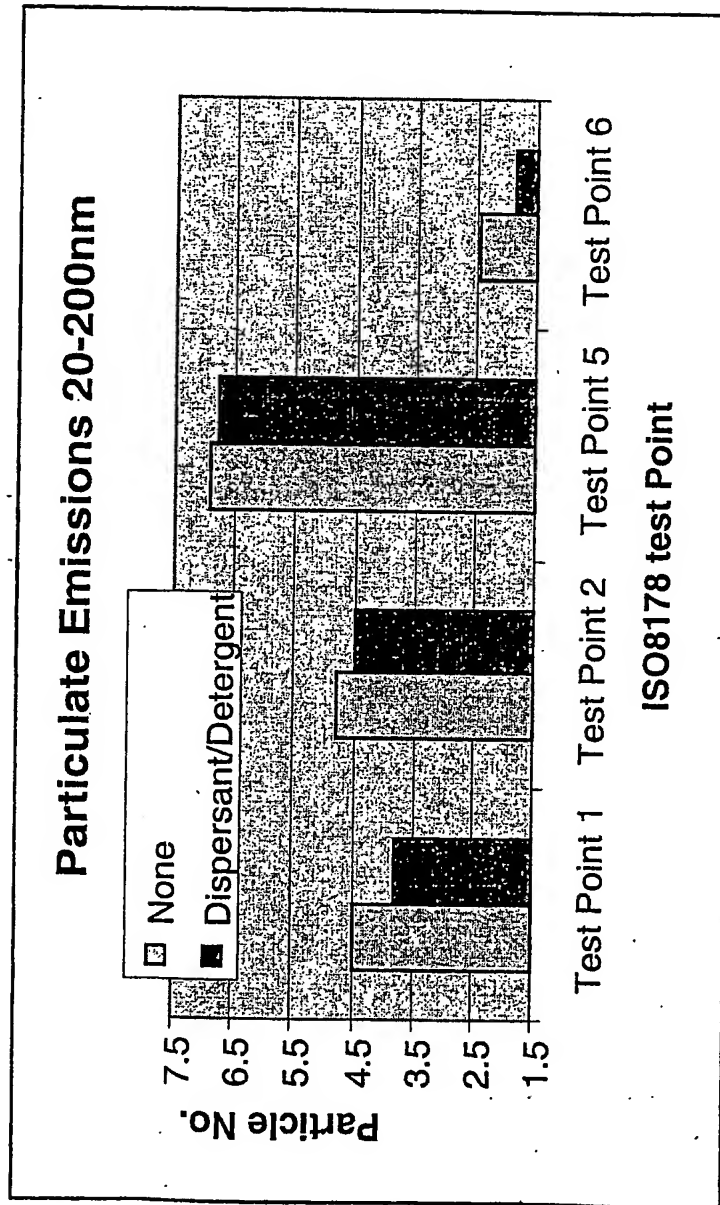


FIGURE 8

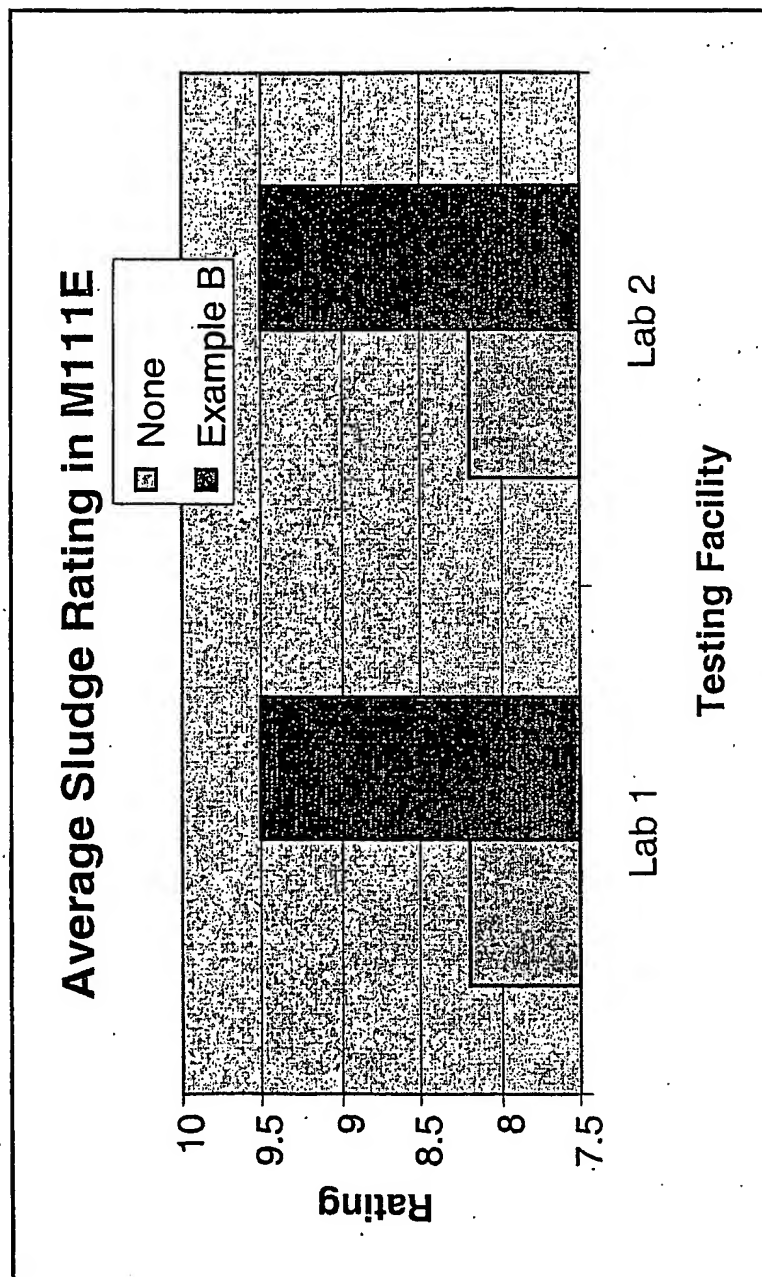


FIGURE 9

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(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
9 October 2003 (09.10.2003)

PCT

(10) International Publication Number
WO 2003/083020 A3

(51) International Patent Classification⁷: **C10M 163/00**,
167/00, C10L 1/22 // C10N 40:25

(21) International Application Number:
PCT/US2003/011199

(22) International Filing Date: 28 March 2003 (28.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/368,354 28 March 2002 (28.03.2002) US
60/441,012 17 January 2003 (17.01.2003) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
22 January 2004

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WO 2003/083020 A3

(54) Title: METHOD OF OPERATING INTERNAL COMBUSTION ENGINE BY INTRODUCING DETERGENT INTO COMBUSTION CHAMBER

(57) Abstract: In a method operating an internal combustion engine, a nitrogen-containing detergent composition is introduced into a combustion chamber of the engine wherein the detergent composition can improve the performance of both a fuel composition and a lubricating oil of the engine. The detergent composition contains (A) a reaction product of a hydrocarbyl-substituted acylating agent and an amine, (B) a hydrocarbyl-substituted amine, (C) a Mannich reaction product, (D) a high molecular weight polyetheramine, or (E) a mixture thereof.

INTERNATIONAL SEARCH REPORT

Inter Application No
PC1705 03/11199

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M163/00 C10M167/00 C10L1/22
//C10N40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10M C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 634 951 A (COLUCCI WILLIAM J ET AL) 3 June 1997 (1997-06-03) abstract column 1, line 29 - column 2, line 7 column 8, lines 5-15 column 8, lines 20-25 column 9, lines 20-23	1-3,6,8, 10-14
X	US 4 231 759 A (UDELHOFEN JOHN H ET AL) 4 November 1980 (1980-11-04) abstract column 1, lines 6-64 column 3, lines 16-63 column 5, line 63 - column 6, line 6 table I example II example III	1-3,6,8, 10-14

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

26 September 2003

Date of mailing of the international search report

21.11.03

Name and mailing address of the ISA

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Perakis, N.

INTERNATIONAL SEARCH REPORT

Inter Application No
PC1/US 03/11199

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GB 2 010 324 A (CHEVRON RES) 27 June 1979 (1979-06-27) abstract page 2, line 106 - page 2, line 112 -----</p>	<p>1-3,6,8, 10-14</p>

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

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1-4, 8, 10-14

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-4,8,10-14

A method of operating an internal combustion engine comprising the introduction in the combustion chamber of a compound (A) alone or in combination with an other N-containing compound selected from (A) to (D).

2. claims: 1-3,5,9-14

A method of operating an internal combustion engine comprising the introduction in the combustion chamber of a compound (B) either alone or in combination of an other N-containing compound (A)-(D).

3. claims: 1-3,6,8,10-14

A method of operating an internal combustion engine comprising the introduction in the combustion chamber of a compound (C) either alone or in combination with an other N-containing compound (A) to (D).

4. claims: 1,7-14

A method of operating an internal combustion engine comprising the introduction in the combustion chamber of a compound (D) either alone or in combination with an other N-containing compound (A)-(D).

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter

Application No

PC1/US 03/11199

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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